【Detailed Description of the Invention】

【0001】

【Field of Art belonging to the Invention】

The invention relates to a polycarbonate copolymer containing bisphenols with a specific structure and, more specifically, relates to a novel polycarbonate copolymer with excellent optical properties.

【0002】

【Prior Art】

A polycarbonate resin to be produced by reaction of 2,2-bis(4-hydroxyphenyl)propane (so-called bisphenol A) and phosgene or a carbonic acid ester forming compound is applied to wide uses because it has good transparency, excellent heat resistance and excellent mechanical properties.

【0003】

However, with expansion into various uses, characteristics to be required for a polycarbonate resin become severe, so that development of a polycarbonate resin with more excellent performances has been desired. Particularly, when a molded article is obtained using conventional polycarbonate resin by injection molding, the molded article causes readily large stress optical strain, i.e., large birefringence. There is a problem that it is not suitable to a base material of instrument for optics in which optical strain becomes problematic.

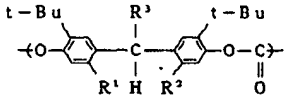
【0004】

Homopolymer comprising a repeating unit represented by the following formula (I) has been known for a long time and is disclosed in USP 3510507, EP1308521, USP3655718, USP369132, USP3737486, USP3773812, Japanese Patent Publication Nos.52-15538A, 52-43847A, 52-58747A, 52-128359A, 53-92864A, 53-110642A and 54-29358A. Its

mechanical strength is low. It has been used mainly as a stabilizer.

【0005】

【Chemical 5】



... (1)

【0006】

Japanese Patent Publication No.52-148594A discloses that a carbonate oligocopolymer less than 20 of sum (total polymerization number) of the repeating unit represented by the above-mentioned formula (I) is used a stabilizer. Further, Japanese Patent Publication No.59-120206A discloses a selective separation membrane comprising the repeating unit represented by the above-mentioned formula (I) and a repeating unit from bisphenol A.

【0007】

Thus, under the present situation, the art concerning a copolymer with excellent optical properties comprising the repeating unit represented by the above-mentioned formula (I) has not been established.

【0008】

【Problem to be solved by the Invention】

Thus, an object of the invention is to provide a polycarbonate copolymer with excellent optical properties. Other object of the invention is to provide a polycarbonate copolymer with both good transparency and a small photoelastic constant. Further other object of the invention is to provide a polycarbonate copolymer with such excellent optical properties as described above and good moldability, good heat resistance and excellent mechanical properties. Further other object of the invention is to provide a process for producing industrially advantageously and efficiently a polycarbonate copolymer. Further other object of the

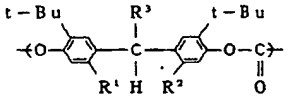
invention is to provide an information transmission medium or an information recording medium using the above-mentioned polycarbonate copolymer as a base material. Other objects and merits of the invention become clear by the following explanation.

【0009】 ～ 【0014】

【Means for solving the Problem】

According to the invention, the above-mentioned object and merits of the invention are attained by a polycarbonate copolymer comprising 5 to 95 mol% of the first repeating unit represented by the following formula (Ⅰ) and 95 to 5 mol% of the second repeating unit to be selected from the following formulas (Ⅱ)-a and (Ⅱ)-b and having a reduced viscosity (η_{sp}/C) of at least 0.3 dl/g at 20℃ in a 0.5g/dl concentration solution used methylene chloride as a solvent a photoelastic constant of 70×10^{-13} cm^2/dyne or below and a glass transition temperature of at least 95℃;

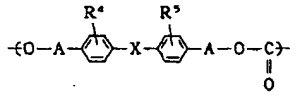
[Chemical 6]



··· (1)

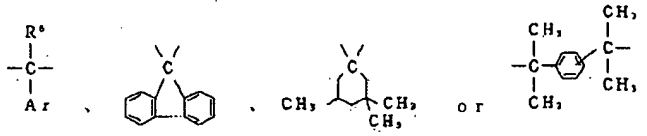
wherein R^1 and R^2, each the same or different, are a methyl group or an ethyl group and R^3 is an alkyl group of 1 to 6 carbon atoms ;

[Chemical 7]



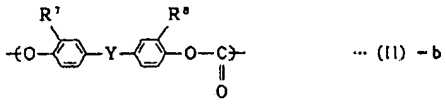
··· (II) -a

wherein R^4 and R^5, each the same or different, are a hydrogen atom, an alkyl group of 1 to 6 carbon atoms or an aryl group of 6 to 10 carbon atoms and X is ;



wherein R^6 is an alkyl group of 1 to 6 carbon atoms ; Ar is an aryl group of 6 to 10 carbon atoms and A is a single bond or an alkylene group of 2 to 4 carbon atoms ;

【Chemical 8】



··· (II) -b

wherein R^7 and R^8, each the same or different, are an alkyl group of 1 to 6 carbon atoms or an aryl group of 6 to 10 carbon atoms and Y is ;

or

wherein R^9 and R^{10}, each the same or different, are a hydrogen atom, an alkyl group of 6 to 10 carbon atoms or an aryl group of 6 to 10 carbon atoms.

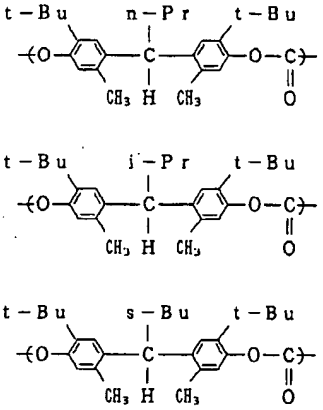
【0015】

The polycarbonate copolymer of the invention consists essentially of the first repeating unit of the above-mentioned formula (I) and the second repeating unit selected from the above-mentioned formulas (Ⅱ)-a and (Ⅱ)-b

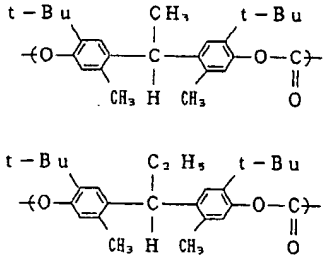
【0016】 ～ 【0022】

In the above-mentioned formula (I), R^1 and R^2, each the same or different, are a methyl group or an ethyl group. R^3, R^4 and R^5 are an alkyl group of 1 to 6 carbon atoms which may be linear or branched and examples thereof include a methyl group, an ethyl group, n-propyl group, an iso-propyl group, a n-butyl group, an iso-butyl group, a sec-butyl group, a tert-butyl group, a n-pentyl group and a n-hexyl group. Examples of the repeating unit represented by the above-mentioned formula (I) include;

【Chemical 9】

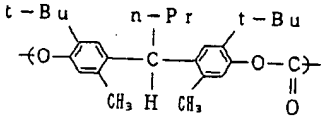


【Chemical 10】



Particularly,

【Chemical 11】



is preferable

【0023】

In the above-mentioned formula (II)-a, R^4 and R^5, each the same or different, are a hydrogen atom, an alkyl group of 1 to 6 carbon atoms or an aryl group of 6 to 10 carbon atom.

【0024】

The alkyl group of 1 to 6 carbon atoms may be linear or branched and

its examples include a methyl group, an ethyl group, a n-propyl group, an iso-propyl group, a n-butyl group, an iso-butyl group, a sec-butyl group, a tert-butyl group, a n-pentyl group and n-hexyl group.

【0025】

Examples of the aryl group of 6 to 10 carbon atoms include a phenyl group, a tolyl group, a xylyl group a cumyl group and a naphthyl group.

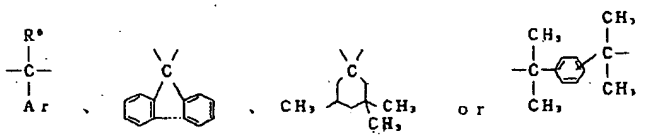
【0026】

In the group of -A-O-, A is a single bond and represents as a whole an oxy group (-O-) or a group of -O- (-an alkyl group of 2 to 4 carbon atoms) -O-, Examples of an alkylene group in the letter group include 1,2-ethylene, 1,1-ethylene, 1,3-trimethylene, 1,2-propylene and 1,4-tetramethylene.

【0027】 ～ 【0029】

The group represented by X is:

【Chemical 12】



【0030】

R^6 is an alkyl group of 1 to 6 carbon atoms and Ar is an aryl group of 6 to 10 carbon atoms and each example thereof is the same as that of the above-mentioned R^4.

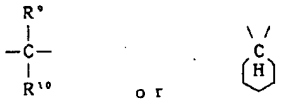
【0031】

In the above-mentioned formula (Ⅱ)-b, R^7 and R^8, each the same or different, are an alkyl group of 1 to 6 carbon atoms or an aryl group of 6 to 10 carbon atoms. Each of examples of the alkyl group of 1 to 6 carbon atoms and the aryl group of 6 to 10 carbon atoms is the same as that those of the above-mentioned R^4.

【0032】 ～ 【0034】

The group represented by Y is;

【Chemical 13】



【0035】

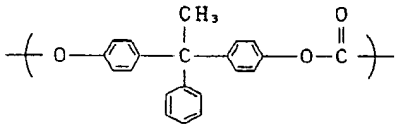
R^9 and R^{10}, each the same or different, are a hydrogen atom, an alkyl group of 1 to 6 carbon atoms or an aryl group of 6 to 10 carbon atoms. Examples thereof are the same as those of the above-mentioned R^4.

【0036】 ～ 【0041】

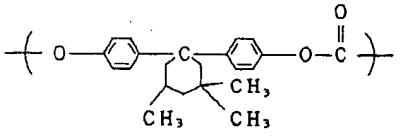
Example of the second repeating unit include, preferably;

【Chemical 14】

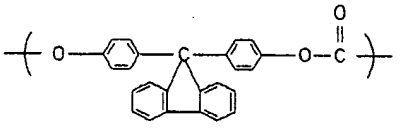
(A)



(B)

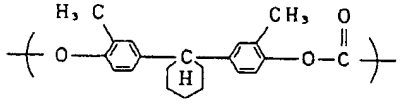


(C)

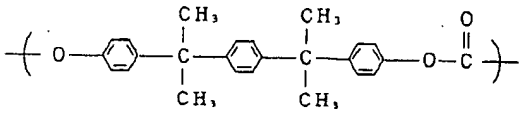


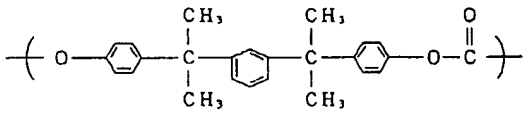
【Chemical 15】

(D)

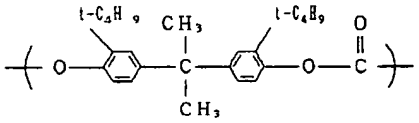


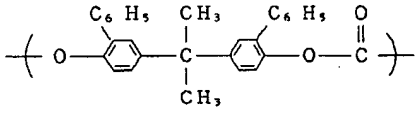
(E)



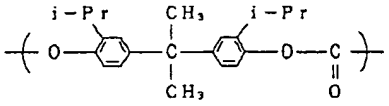
(F) 

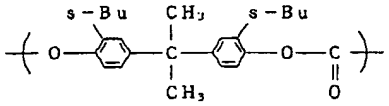
【Chemical 16】

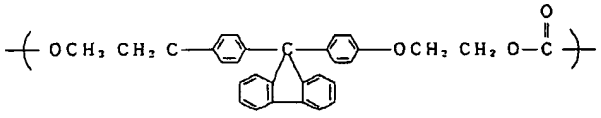
(G) 

(H) 

【Chemical 17】

(I) 

(J) 

(K) 

【0042】

The second repeating units (A) to (K) represented by the formulas (Ⅱ)-a and (Ⅱ)-b may be present in at least one species thereof in the polycarbonate copolymer of the invention.

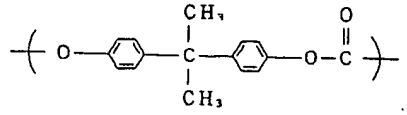
【0043】

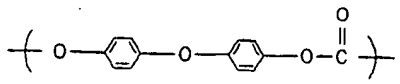
The polycarbonate copolymer of the invention comprises 5 to 95 mol% of the first repeating unit represented by the above-mentioned formula (Ⅰ) and 95 to 5 mol% of the second repeating unit represented by the above-mentioned formula (Ⅱ). When the first repeating unit is below 5 mol%, intended optical properties cannot be obtained. When it is above 95 mol%, mechanical strength and polymerization are insufficient. The first repeating unit is preferably 7 to 93 mol%, more preferably 10 to 80 mol% and the most preferably 15 to 75 mol%. The second repeating unit is preferably 93 to 7 mol%, more preferably 90 to 20 mol% and the most preferably 85 to 25 mol%.

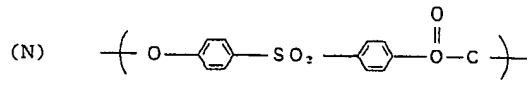
【0044】 ～ 【0046】

Further, in the invention, the following third repeating unit may be present in the copolymer. The combination of the second repeating unit selected from the group consisting of the above-mentioned (A) to (K) and the third repeating unit selected from the group consisting of the following (L) to (N) is particularly preferable. In the polycarbonate copolymer, the sum total of the first repeating unit and the second repeating unit is at least 50 mol% ; the third repeating unit is 50 mol% or below and the ratio(mol%) of the second repeating unit to the first repeating unit is represented by the following formula ;

【Chemical 18】

(L) 

(M) 

(N) 

【Numerical 2】

Second repeating unit (mol%)/first repeating unit (mol%) = 5/95 to 95/5

It is preferable that the ratio is 25/75 to 8/15.

【0047】

The polycarbonate copolymer of the invention has a reduced viscosity (η_{SP}/C) of at least 0.3 dl/g at 20℃ in a 0.5 g/dl concentration solution used methylene chloride as a solvent. Preferable reduced viscosity is in the range of 0.3 dl/g to 1.0 dl/g.

【0048】

The polycarbonate copolymer of the invention has a photolastic constant of $70\times10^{-13}cm^2$/dyne or below. Since it is known that $1\times10^{-13}cm^2$/dyne is 1 Brewsters (B), $70\times10^{-13}cm^2$/dyne or below can be set forth as 70B or below.

【0049】 ～ 【0050】

Regarding photoelastic constant, a tensile stress with different magnitude to each other was imposed on a test piece (10mm×100mm×1mm) of the polycarbonate copolymer in the direction of its length and generated birefringence index is measured. Photoelastic constant is calculated from the following formula ;

【Numerical 3】

$$C=(n_1-n_2)/(\sigma_1-\sigma_2)$$

wherein C is photoelastic constant ; n_1 and n_2 are birefringence index in first and second tensile stress, respectively and σ_1 and σ_2 each are first and second tensile stress (dyne/cm^2). Photoelastic constant is preferably

60B or below and more preferably 50B or below.

【0051】

Further, the polycarbonate copolymer of the invention has a glass transition of at least 95℃, preferably at least 110℃ and more preferably at least 120℃.

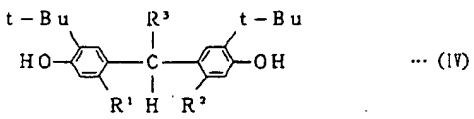
【0052】

The polycarbonate copolymer of the invention can be industrially advantageously produced according to the following process for production.

【0053】 ～ 【0059】

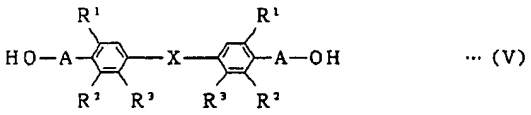
That is, the polycarbonate copolymer can be produced by melt polycondensing bisphenols represented by the following formulas (Ⅳ) and (Ⅴ) and diaryl carbonates represented by the following formula (Ⅵ) in 5 to 95 mol% of the compound of the above-mentioned formula (Ⅳ) and 95 to 5 mol% of the compound of the above-mentioned formula (Ⅴ) based on the sum total of the compound of the above-mentioned formula (Ⅳ) and the compound of the above-mentioned formula (Ⅴ) and in the proportion of 1.0 to 1.3 mol of the compound of the above-mentioned formula (Ⅳ) to total 1 mol of the compound of the above-mentioned formula (Ⅳ) and the compound of the above-mentioned formula (Ⅴ), thereby producing a polycarbonate with a reduced viscosity of at least 0.3 dl/g.

[Chemical 19]



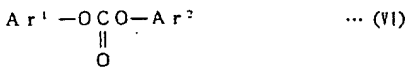
··· (Ⅳ)

[Chemical 20]



… (V)

[Chemical 21]



… (VI)

【0060】

Examples of the compound represented by the above-mentioned formula (Ⅳ) include ;

1,1-bis(3-tert-butyl-4-hydroxy-6-methylphenyl)-n-butane,

1,1-bis(3-tert-butyl-4-hydroxy-6-methylphenyl)-2-methylpropane,

1,1-bis(3-tert-butyl-4-hydroxy-6-methylphenyl)-2-methylbutane,

1,1-bis(3-tert-butyl-4-hydroxy-6-methylphenyl)ethane and

1,1-bis(3-tert-butyl-4-hydroxy-6-methylphenyl)propane, among which

1,1-bis(3-tert-butyl-4-hydroxy-6-methylphenyl)-n-butane is preferable.

【0061】

Examples of the compound represented by the above-mentioned formula (V) include ;

1- phenyl,

1,1-bis(4-hydroxyphenyl)ethane,

1,1-bis(4-hydroxyphenyl),

3,3,5-trimethylcyclohexane,

1,1-bis(4-hydroxyphenyl)fluorene,

1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane,

1,4-bis[2-(4-hydroxyphenyl)propyl]benzene,

1,3-bis[2-(4-hydroxyphenyl)propyl]benzene,

2,2-bis(3-tert-butyl-4-hydroxyphenyl)propane,

2,2-bis(4-hydroxy-3-phenyl)propane,

1,1-bis[4-(2-hydroxyethyloxy)phenyl]fluorene,

2,2-bis(4-hydroxyphenyl)propane,

bis(4-hydroxyphenyl)ether and

bis(4-hydroxyphenyl)sulfone.

【0062】

In the above-mentioned formula (VI), $Ar^1$and Ar^2 each the same or different, are a phenyl group or a naphthyl group, which may be substituted by a chlorine atom, an alkyl group of 1 to 6 carbon atoms, a methoxycarbonyl group or an ethoxycarbonyl group. The substituent may be at least one species.

【0063】

Examples of the alkyl group of 1 to 6 carbon atoms include the same examples of R^1 in the formula (I).

【0064】

Examples of the compound represented by the formula (VI) include diphenyl carbonate, di-p-tolyl carbonate, phenyl-p-tolyl carbonate, di-p-chlorophenyl carbonate, di(2-methoxycarbonylphenyl) carbonate, phenyl-2-methoxycarbonylphenyl carbonate, di(2-ethoxycarbonylphenyl) carbonate and dimecuthyl-p-carbonate.

【0065】

The process of the invention is carried out in the proportion of 1.0 to 1.3 mol of diaryl carbonates of the above-mentioned formula (VI) to total 1 mol of the compound of the above-mentioned formula (IV) and the compound of the above-mentioned formula (V). In the range, preferable proportion is 1.005 to 1.10 mol.

【0066】

The compound of the above-mentioned formula (Ⅳ) of 5 to 95 mol% and the compound of the above-mentioned formula (Ⅴ) of 95 to 5 mol% based on the sum total of the compound of the above-mentioned formula (Ⅳ) and the compound of the above-mentioned formula (Ⅴ) as diol components are used. Preferable proportion is 10 to 90 mol% of the compound of the formula (Ⅳ) and 90 to 10 mol% of the compound of the formula (Ⅴ).

【0075】

The novel polycarbonate copolymer of the invention is usefully applied, for example, to a base material of an information transmission medium such as optical fiber and a base material of information recording medium such as optical disc.

【0077】

[Example 1]

306 parts by weight (0.8 mol) of 1,1-bis(3-tert-butyl-4-hydroxy-6-methylphenyl)-n-butane and 68 parts by weight (0.2mol) of 2,2-bis(3-tert-butyl-4-hydroxyphenyl)propane as diol components, 225 parts by weight (1.05 mol) of diphenyl carbonate as a carbonic acid ester forming compound and 9.1×10^{-3} parts by weight of tetramethylammonium hydroxide as a catalyst and 4×10^{-4} parts by weight of sodium hydroxide was charged to a reactor vessel equipped with a stirrer, a distiller and a vacuum apparatus and its interior was replaced with nitrogen and then heat melting was conducted. After stirring for 30 minutes, its interior pressure was gradually reduced while raising its interior temperature to 180℃ and the reaction was performed for 30 minutes under 100 mmHg while distilling off produced phenol.

【0078】

Then, after raising its interior temperature to 200℃, its interior pressure was gradually reduced and the reaction was performed under 50

mmHg for 20 minutes while distilling off phenol. Raise of temperature and reduction of pressure were gradually further conducted up to 220℃ /30 mmHg and the reaction was performed at its temperature under its pressure for 20 minutes. Raise of temperature and reduction of pressure were repeated in the same procedure as described above further up to 240℃/10mmHg, 280℃/1mmHg or below to continue the reaction. Finally, the reaction was performed in 280℃/1mmHg or below for 2 hours.

【0079】

A polymer thus obtained had a reduced viscosity [η_{sp}/C] of 0.35 dl/g at 20℃ in a solution used methylene chloride as a solvent. The polymer thus obtained had a glass transition temperature of 150℃ in the measurement by a thermal analyzer (2000 type DSC), manufactured by Du Pont, Co. Further the polymer was molded to a film of thickness 100 μm. It had a photoelastic constant of 46×10^{-13}cm^2/dyne in the measurement by a photoelastic measuring apparaturs (PA-150) manufactured by Riken Keiki Co, and its value was low. (The same measurement was conducted also in the below Examples and Comparative Examples).

【0093】

[Effect of the Invention]

As described above, the polycarbonate copolymer of the invention has smaller photoelastic constant, smaller birefringence due to low molding stress and more excellent optical properties than those of conventional polycarbonate resin.

【0094】

The polycarbonate to be produced from bisphenol with specific substitution structure and a carbon acid ester forming compound was inferior in mechanical properties. As in the invention, a polycarbonate with excellent optical properties, both sufficient heat resistance and

mechanical strength can be obtained by copolymerizing several kinds of specific bisphenols.

【0095】

Therefore, the polycarbonate of the invention is utilized as a base material of various industrial instruments including a base material for optical instrument such as optical disc.